

Effect of Surfactant on Oxidation of Acetaldehyde by KMnO_4 in Acidic Medium: A Kinetic Approach

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Abstract

A kinetic study of oxidation of acetaldehyde by KMnO_4 in acidic medium in the absence and presence of cationic surfactant, cetylpyridinium bromide (CPB) under pseudo first order reaction condition was investigated following Ostwald's isolation method. Order of reaction is found to be first with respect to oxidant and fractional with respect to acetaldehyde. The rate of reaction increase with increases in concentration of substrate, acid and CPB. The data has been determined in the light of Zucker-Hammett and Bunnett hypotheses.

The effect of [CPB] on the reaction rate was studied and fitted to Piszkiwicz model. The effect of temperature on the reaction has been verified using Arrhenius plot. From the experimental results, thermodynamic activation parameters are evaluated and a plausible reaction mechanism is proposed. Again the effect of variation of salts concentration on the rate of reaction has been studied in both the conditions.

Keywords: Acetaldehyde, cetyl pyridinium bromide (CPB), KMnO_4 , pre-micellar catalysis.

Introduction

Oxidation reaction is a key reaction for the synthesis of many organic compounds⁸. The oxidation of aldehyde by different oxidants has been studied by several researchers.^{1-4,11,14,17} Some researchers¹⁹ observed an easy oxidation procedure for aromatic aldehydes by potassium bromate – bromide reagent in presence of hydrochloric acid catalyst and some other scientists¹⁵ studied the mechanism of oxidation of aliphatic aldehydes by quinolinium chlorochromate (QCC) in dimethyl sulphoxide (DMSO). Kinetics and mechanism of oxidation of methoxy benzaldehyde by benzimidazolium fluorochromate in an aqueous acetic acid medium also been investigated¹³.

The conversion of aldehyde into carboxylic acid is one of the most important transformations in organic synthesis. Wide variety of oxidants has been used for the oxidation reaction but KMnO_4 is the most important and widely used oxidizing agent in several oxidation reactions because of its variable oxidation state, strong oxidizing property and its ecofriendly nature. Several researchers have performed the oxidation of organic compounds by KMnO_4 but limited literature is available on the oxidation of aldehyde by KMnO_4 in

presence of surfactant. Today micellar catalysis has become a very important field for investigation of several reactions because of good catalytic efficiency like enzymatic reactions in biological system.

Material and Methods

All stock solutions were prepared in double distilled water and chemicals used for kinetic study were of A. R. grade. KMnO_4 solution was stored in dark brown glass stoppered bottle covered with black paper to protect from sunlight. The reaction started with the addition of KMnO_4 to thermostated solution of reaction mixture. Effect of a particular reactant concentration was studied by varying its concentration keeping the concentration of all other reactants constant. The reaction was monitored by UV-Visible spectrophotometer 118 Systronic at 520 nm wavelength at various intervals of time.

Results and Discussion

Effect of $[\text{KMnO}_4]$ on the reaction rate: To study the effect of potassium permanganate on the oxidation of acetaldehyde, the concentration of KMnO_4 is varied at constant concentrations of substrate, acid and surfactant. As the KMnO_4 concentration increases, first order rate constant value remains almost constant (table 1). A plot of $\log(a-x)$ versus time gives straight line in both the conditions and plot between $\log k$ and $\log [\text{KMnO}_4]$ was also straight line (Fig. 1) which indicates that the order of reaction is first with respect to $[\text{KMnO}_4]$.

Effect of [Acetaldehyde] on the reaction rate: The oxidation of acetaldehyde by potassium permanganate is studied at different concentrations of acetaldehyde keeping constant concentration of KMnO_4 , CPB and H_2SO_4 . The observed rate of reaction increases with increase in concentration of acetaldehyde (table 2). A plot of $\log k$ versus $\log [\text{CH}_3\text{CHO}]$ is linear and order of reaction is fractional with respect to acetaldehyde in both the cases (fig. 2). Michaelis-Menten plot^{10,22} gives a straight line with an intercept showing the formation of an intermediate complex during the reaction (fig. 3).

Effect of $[\text{H}_2\text{SO}_4]$ on the reaction rate: The variation of $[\text{H}_2\text{SO}_4]$ was studied at constant $[\text{KMnO}_4]$, $[\text{CH}_3\text{CHO}]$ and temperature. The rate of reaction increases with increase in concentration of acid in both the cases (table 3). A plot of $\log k$ versus $\log [\text{H}^+]$ is found to be linear with positive slope indicating the rate of reaction is directly proportional to H_2SO_4 concentration in the absence and presence of CPB (fig. 4).

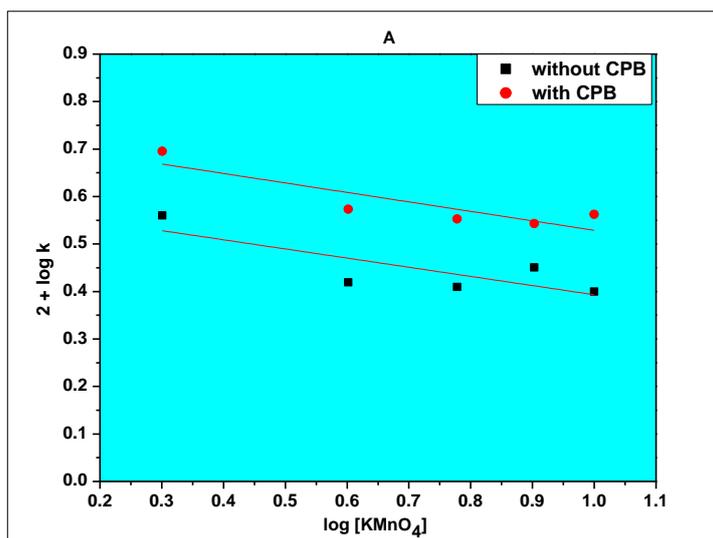


Fig. 1: Effect of [KMnO₄]

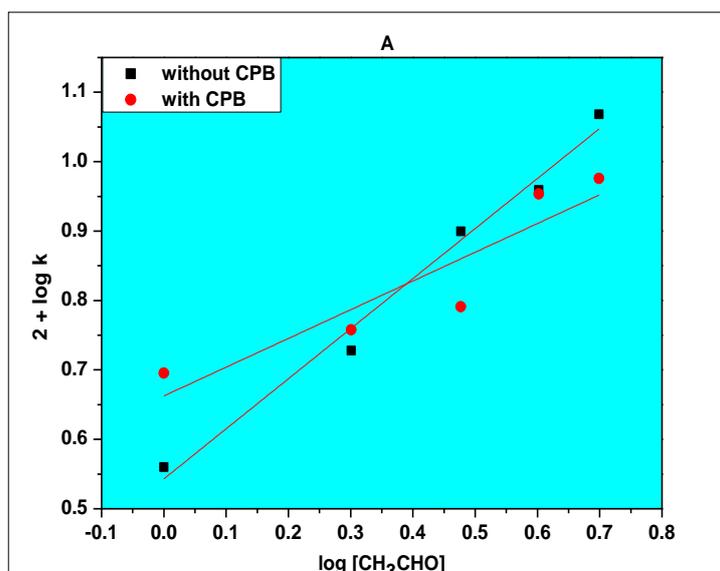


Fig. 2: Effect of [CH₃CHO]

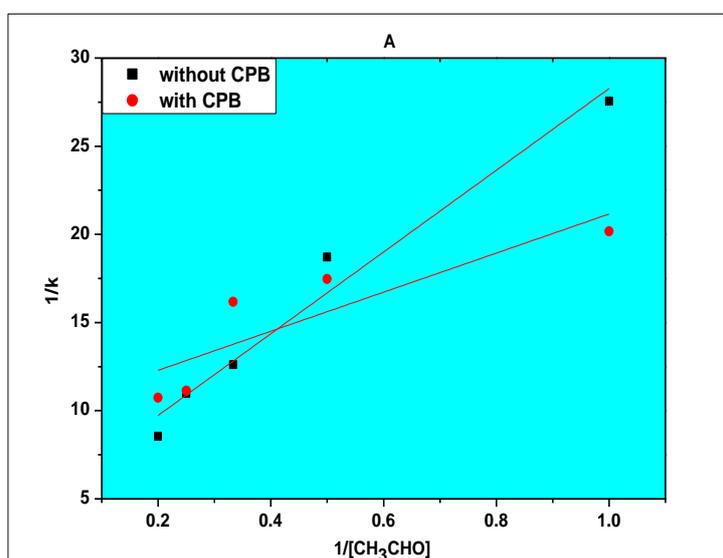


Fig. 3: Michaelis-Menten plot

The Zucker Hammett hypothesis was applied to study the role of H^+ ion on the oxidation reaction, the plot of $\log k$ versus H_0 and $\log k$ versus $\log [H^+]$ gives linear relation (Fig. 5 and 6) and shows that the reaction is acid catalysed. The Zucker-Hammett plots have not given the ideal slope value unity. The deviation from unit slope increased the applicability of Bunnett plot (Fig. 7 and 8). These plots are also straight line graphs and their slope values (i.e. ω and ω^*) indicate the involvement of H_2O molecule in rate determining step as a proton transfer agent. These slope values are summarised in table 4.

Effect of [CPB] on the reaction rate: To study the effect of cationic surfactant i.e. CPB on the oxidation of acetaldehyde, experiments were conducted at different concentrations of CPB keeping constant concentration of substrate, oxidant and acid under pseudo first order reaction condition. The value of catalytic constant (k_c) was calculated and is found constant for different concentrations of CPB. It is observed that the rate of reaction increases with increase in concentration of surfactant (table 5).

Table 1
Effect of $[KMnO_4]$

$[CH_3CHO] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $[H_2SO_4] = 0.25 \text{ mol dm}^{-3}$, $[CPB] = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $T = 298 \text{ K}$					
$[KMnO_4] \times 10^{-5}$ (mol dm^{-3})	k (min^{-1}) (without CPB)	k (min^{-1}) (with CPB)	$\log [KMnO_4]$	$2 + \log k$ (without CPB)	$2 + \log k$ (with CPB)
2	0.036	0.050	0.301	0.560	0.695
4	0.026	0.037	0.602	0.419	0.573
6	0.026	0.036	0.778	0.409	0.553
8	0.028	0.035	0.903	0.451	0.543
10	0.025	0.037	1.000	0.400	0.562

Table 2
Effect of [Acetaldehyde]

$[KMnO_4] = 2 \times 10^{-5} \text{ mol dm}^{-3}$, $[H_2SO_4] = 0.25 \text{ mol dm}^{-3}$, $[CPB] = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $T = 298 \text{ K}$					
$[CH_3CHO] \times 10^{-3}$ (mol dm^{-3})	k (min^{-1}) (without CPB)	k (min^{-1}) (with CPB)	$\log [CH_3CHO]$	$2 + \log k$ (without CPB)	$2 + \log k$ (with CPB)
1	0.036	0.049	0	0.56	0.695
2	0.053	0.057	0.301	0.728	0.758
3	0.079	0.061	0.477	0.899	0.791
4	0.091	0.089	0.602	0.959	0.954
5	0.117	0.094	0.699	1.068	0.976

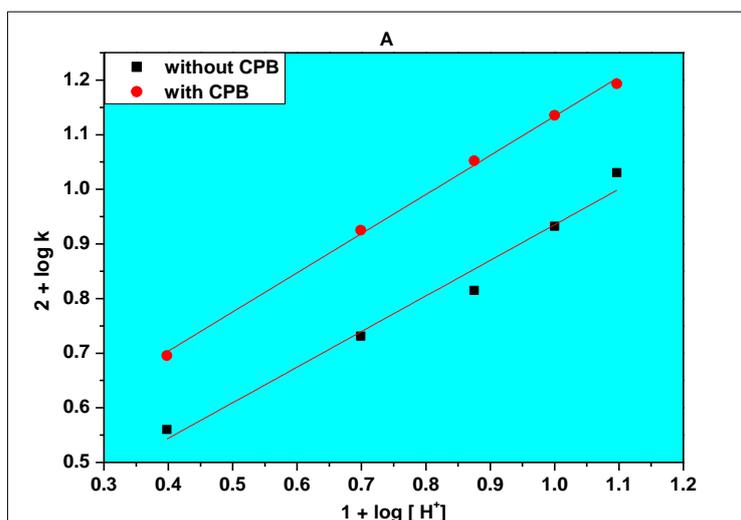


Fig. 4: Effect of $[H_2SO_4]$

Table 3
Effect of [H₂SO₄]

[CH ₃ CHO] = 1×10 ⁻³ mol dm ⁻³ , [KMnO ₄] = 2×10 ⁻⁵ mol dm ⁻³ , [CPB] = 1×10 ⁻⁴ mol dm ⁻³ , T = 298 K					
[H ₂ SO ₄] (mol dm ⁻³)	k (min ⁻¹) (without CPB)	k (min ⁻¹) (with CPB)	1 + log [H ₂ SO ₄]	2 + log k (without CPB)	2 + log k (with CPB)
0.25	0.036	0.050	0.398	0.560	0.695
0.50	0.054	0.084	0.699	0.731	0.925
0.75	0.065	0.113	0.875	0.815	1.052
1.00	0.086	0.137	1.000	0.932	1.135
1.25	0.107	0.156	1.097	1.031	1.193

Table 4
Correlation of reaction rate with [H⁺]

S. No.	Correlation	Parameters	Slope value
Zucker-Hammett plots			
a.	log k versus H ₀		-0.54
b.	log k versus log [H ⁺]		0.65
Bunnett's plots			
a.	(log k + H ₀) versus -log a _{H₂O}	ω	4.70
b.	(log k - log [H ⁺]) versus -log a _{H₂O}	ω*	2.77

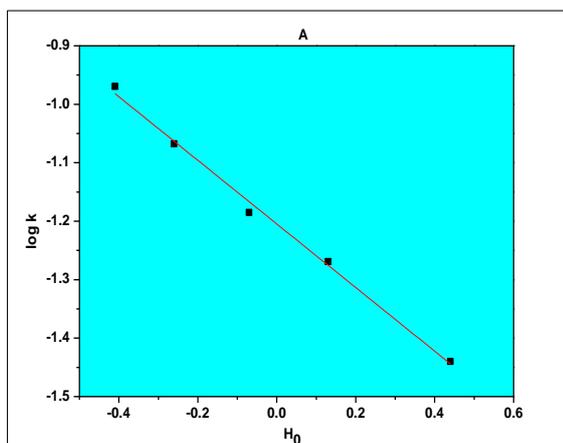


Fig. 5: Zucker-Hammett plot

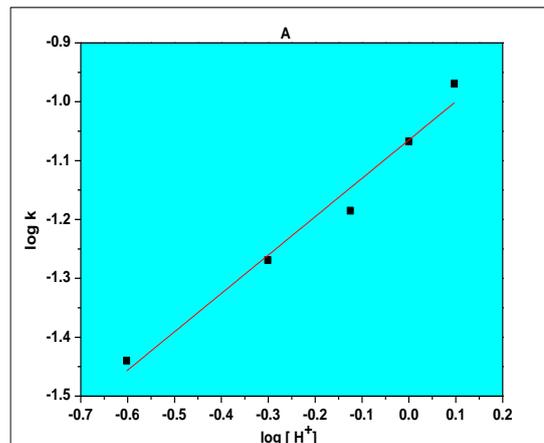


Fig. 6: Zucker-Hammett plot

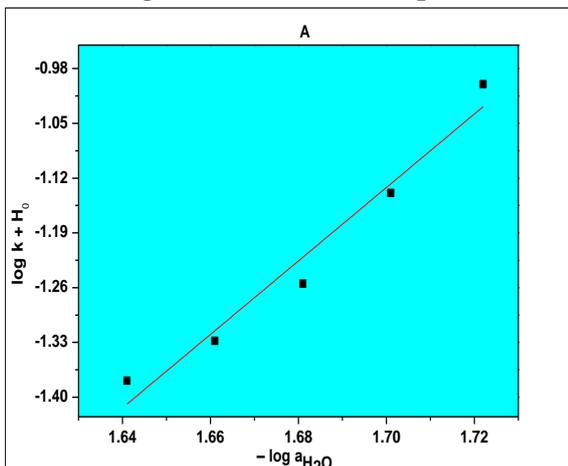


Fig. 7: Bunnett plot

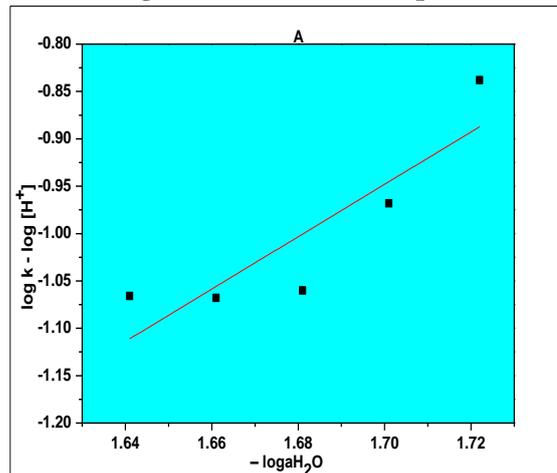


Fig. 8: Bunnett plot

A plot of k versus $[\text{CPB}]$ gives a straight line with positive slope (fig. 9), this shows that surfactant is catalyzing the oxidation reaction. Here the catalysis below CMC indicates the formation of pre-micellar aggregates^{6,16,20}. This pre-micellar catalysis is determined by plotting a Piszkiwicz^{5,9,21} graph between $\log [(k_{\text{obs}} - k_0)/(k_m - k_{\text{obs}})]$ and $\log [\text{CPB}]$ (fig. 10) where k_0 is rate constant in absence of CPB and k_{obs} is rate constant at different CPB concentration. The Piszkiwicz plot gives a straight line with positive slope value. The obtained slope value (n) is the expected value for pre-micellar catalysis (which comes in between 1 and 6). In

this case, the value of slope (n) obtained is 1.643 (fig. 10) which confirms the pre-micellar catalysis.

Effect of temperature on the reaction rate: To study the effect of temperature, reaction has been carried out at five different temperatures from 298 K to 318 K in presence and absence of CPB at constant concentration of all reactants. The observed rate of reaction increases with increase in temperature (table 6) and a plot of rate constant versus temperature is found to be linear (fig. 11).

Table 5
Effect of $[\text{CPB}]$

$[\text{CH}_3\text{CHO}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.25 \text{ mol dm}^{-3}$, $[\text{KMnO}_4] = 2 \times 10^{-5} \text{ mol dm}^{-3}$, $T = 298 \text{ K}$			
$[\text{CPB}] \times 10^{-4}$ (mol dm^{-3})	k (min^{-1})	$\log [\text{CPB}]$	$2 + \log k$
1	0.050	0.00	0.70
2	0.058	0.30	0.77
3	0.071	0.48	0.85
4	0.094	0.60	0.98
5	0.121	0.70	1.08

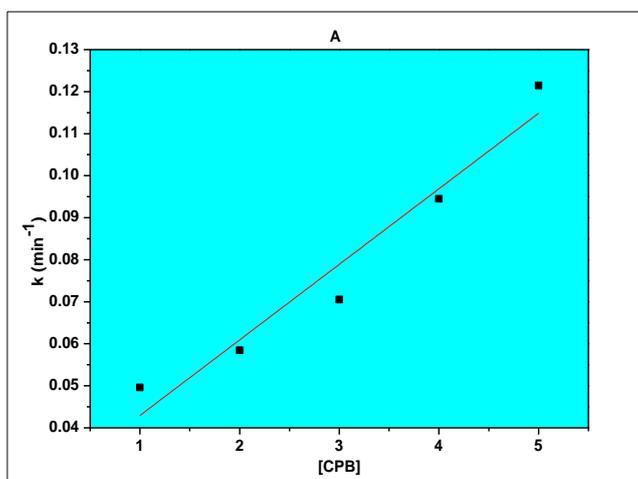


Fig. 9: Effect of $[\text{CPB}]$

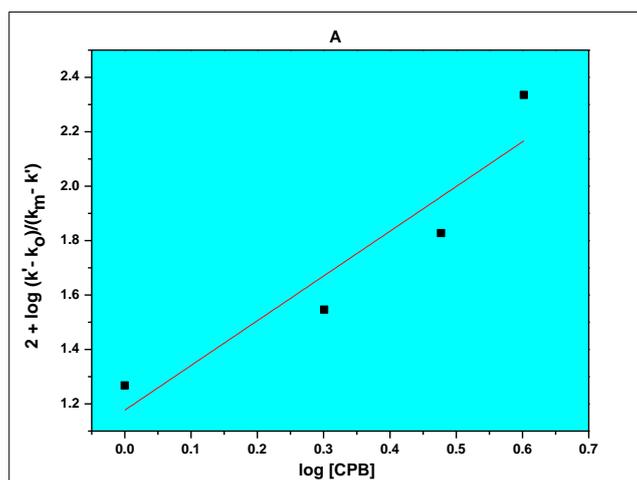


Fig. 10: Piszkiwicz plot

This shows that the rate of reaction depends on the temperature. Thermodynamic activation parameters are calculated and summarised in table 7. Straight line graph with negative slope obtained by plotting $\log k$ versus $1/T$ proved validity of Arrhenius equation^{7,12,18} (fig. 12).

The value of activation energy is positive for both the conditions studied. But the value is higher in the case where

surfactant is used. This may be due to the fact that increase in temperature favours the formation of micellar aggregates below the CMC value. The decrease in negative value of entropy for the reaction in the presence of CPB again reveals the favourable condition for the formation of pre-micellar aggregates with increase in temperature.

Table 6
Effect of Temperature

[CH ₃ CHO] = 1×10 ⁻³ mol dm ⁻³ , [KMnO ₄] = 2×10 ⁻⁵ mol dm ⁻³ , [H ₂ SO ₄] = 0.25 mol dm ⁻³ , [CPB] = 1×10 ⁻⁴ mol dm ⁻³				
Temperature (K)	k (min ⁻¹) (without CPB)	k (min ⁻¹) (with CPB)	2 + log k (without CPB)	2 + log k (with CPB)
298	0.036	0.050	0.56	0.70
303	0.037	0.067	0.56	0.83
308	0.049	0.071	0.69	0.85
313	0.054	0.107	0.74	1.03
318	0.063	0.153	0.80	1.18

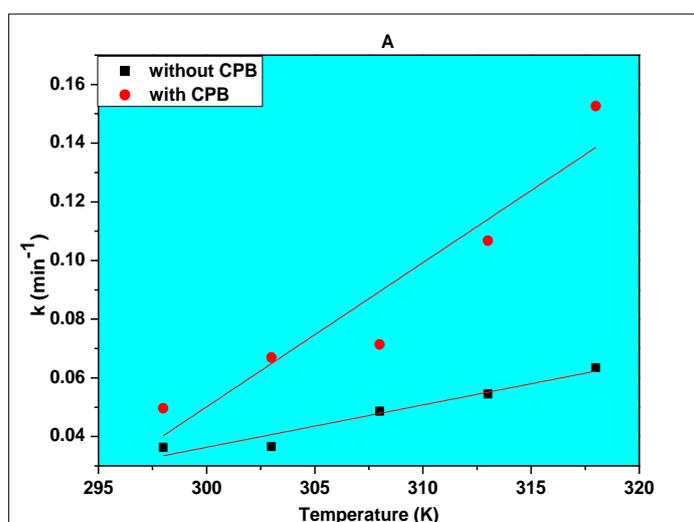


Fig. 11: Effect of Temperature

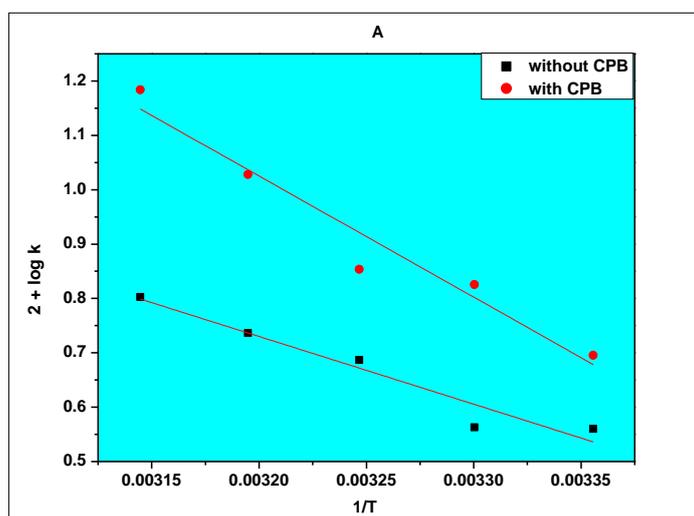


Fig. 12: Arrhenius plot

Table 7
Thermodynamic and activation parameters

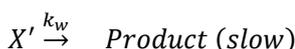
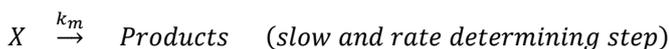
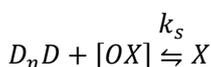
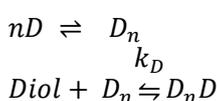
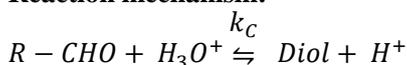
	$\Delta E_a^\#$ (KJ mol ⁻¹)		log pZ	$\Delta H^\#$ (KJ mol ⁻¹)	$-\Delta S^\#$ (Jmol ⁻¹ K ⁻¹)	$\Delta G^\#$ (KJ mol ⁻¹)
	Calculated	Graphical				
without CPB	25.16	23.83	2.97	22.68	188	78.72
with CPB	41.86	42.65	6.03	39.38	129	77.95

Effect of salt: In order to study the effect of salts on the oxidation of acetaldehyde, reactions were conducted at various initial concentrations of salt keeping all other factors constant. The salts taken for the study were KCl, KNO₃, MgCl₂.6H₂O and Mg(NO₃)₂.6H₂O. In the presence of the surfactant (CPB), KCl and MgCl₂ showed an accelerating effect on the reaction rate. But in the absence of the surfactant, these salts have no effect on the reaction rate. It is observed that KNO₃ and Mg(NO₃)₂ have no effect on the reaction rate both in the absence and presence of the surfactant.

Stoichiometry: To determine the stoichiometry of the reaction, experiments were conducted taking excess amount of KMnO₄ over the substrate and allowed to stand at room temperature for 24 hours. The amount of unconsumed KMnO₄ was estimated spectrophotometrically and from the result, it is concluded that 5 moles of substrate (aldehyde) consume 2 moles of KMnO₄. On the basis of the present investigation and literature available, the reaction can be presented as follows:



Reaction mechanism:



where nD is number of surfactant molecules, D_n is pre-micellar aggregates, S₀ is initial concentration of substrate, X is the complex formed between substrate-associated micelle and oxidant and X' is the complex formed without the surfactant.

The overall reaction rate can be written as:

$$-\frac{d[OX]}{dt} = k_w[X'] + k_m[X]$$

By doing appropriate substitution, the total reaction rate can be expressed as:

$$\frac{-d[ox]}{dt} = \frac{[S_0][ox]_0(k'_w + k_m k'_s [D_n])}{1 + k'_s [D_n][S_0]}$$

The above expression explains all experimental findings.

Conclusion

Present work shows that the rate of oxidation of acetaldehyde increases with increase in concentration of acetaldehyde, acid and CPB. Rate of reaction also increases with increase in temperature and Arrhenius condition is proved. The order of reaction is found to be first and fractional with respect to oxidant and acetaldehyde respectively. The formation of an intermediate complex during the reaction has been proved by Michaelis-menten plot.

The involvement of water molecule in the reaction has been proved through Zucker-Hammett and Bunnett plots. Salt studied has no effect in the absence of the surfactant but in the presence of surfactant, the salts show positive effect. The rate of the reaction increases with increase in concentration of surfactant and catalysis has been proved as pre-micellar catalysis.

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